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Multi-field effective Hamiltonian theory

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Abstract

Ideally one would like to analyse the properties of inhomogeneous fluids/Ising-like magnets (e.g., wetting of a fluid phase at a wall or confinement in thin film geometries) using a microscopic Hamiltonian $H[m]$, with $m(\mathbf{r})$ the local order-parameter (number density/magnetization). For many problems, however, this is too difficult and traditionally one has to introduce effective interfacial models based on a collective coordinate $l(\mathbf{y})$ measuring the position of the fluid interface. We review progress made in unifying these approaches using *multi-field* effective Hamiltonian theory which is a powerful new investigative tool. We emphasize: (i) a systematic method for recovering order-parameter correlations $G(\mathbf{r}_1,\mathbf{r}_2)$ from collective coordinate theory, (ii) the role of coupled fluctuations at three dimensional wetting transitions leading to (a) an observable increment to the value of the wetting parameter at complete wetting and (b) an inflation of the mean field regime for local surface response functions at critical wetting, (iii) the derivation of new identities relating moments of G at different positions in the fluid, and (iv) the development of a linear response theory of fluid adsorption at a non-planar wall which predicts roughness-induced first-order wetting transitions. The relevance of these predictions for long-standing controversies surrounding Ising model simulation studies is discussed.

Keywords: Statistical mechanics; Interfacial tension; Wetting transitions; Effective models

1. Introduction

A suitable microscopic starting point for modelling fluid adsorption in systems with short-range forces at a planar wall (situated at $z=0$) is the Landau–Ginzburg–Wilson (LGW) Hamiltonian,

$$H_{\mathrm{LGW}}[m] = \int \mathrm{d}\mathbf{y}\left\{\int_0^\infty \mathrm{d}z\left[\frac{1}{2}(\nabla m)^2 + \phi(m)\right] + \frac{c}{2}m_1^2 - m_1 h_1\right\} \tag{1}$$

based on a local magnetization order parameter $m = m(\mathbf{y},z)$ with $m_1(\mathbf{y})$ the value at the $z=0$ surface. Here $h_1 > 0$ and c are the surface field and enhancement, respectively, while $\phi(m)$ is a

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suitable double-well energy density yielding coexistence between bulk magnetizations $m_\alpha > 0$ and $m_\beta < 0$ for sub-critical temperatures $T < T_c$ and zero bulk field $h = 0$. In the context of wetting theory, however, a direct analysis of this model is not possible except in mean-field MF approximation which ignores fluctuation effects [1]. To include long-wavelength interfacial fluctuations most authors consider effective Hamiltonians of the form [2,3]

$$H[l] = \int \mathrm{d}\boldsymbol{y} \left\{ \frac{1}{2}\left(\Sigma_{\alpha\beta} + \Delta\Sigma(l)\right)(\nabla l)^2 + W(l) \right\} \tag{2}$$

based on a collective coordinate $l(\boldsymbol{y})$ describing the position of the $\alpha\beta$ interface. The binding potential is usually specified as

$$W(l) = \bar{h}l + 2\kappa m_\alpha \tau \mathrm{e}^{-\kappa l} + b\mathrm{e}^{-2\kappa l}, \tag{3}$$

where

$$\tau = \frac{h_1 - cm_\alpha}{c + \kappa};\ \bar{h} = (m_\beta - m_\alpha)h;\ \ b > 0 \tag{4}$$

and κ is the inverse correlation length of the bulk α phase adsorbed at the wall–β interface. We distinguish between (a) complete and (b) critical wetting transitions corresponding to the divergence of the adsorption $\langle l \rangle$ and transverse correlation length $\xi_\parallel$ for (a) $\bar{h} \to 0$ for $\tau > 0$ and (b) $\tau \to 0^-$ for $\bar{h} = 0$, respectively. We shall focus on the behavior at the upper critical dimension $d = 3$ where including fluctuation effects does not alter the MF critical wetting phase boundary $\tau = 0$ for all pertinent situations. Minimization of $W(l)$ recovers the MF adsorption and free energy. Note that we have included a possible weak position-dependent correction term $\Delta\Sigma(l)$ to the free stiffness coefficient $\Sigma_{\alpha\beta}$ following the work of Parry [3] and Fisher and Jin [4] who initiated recent reassessments of effective Hamiltonian theory.

In this article we describe the central theorems, results and predictions of multi-field effective Hamiltonian theory which form a synthesis between MF and generalized collective coordinate approaches. Our main motivation here is the resolution of three problems of wetting theory.

Problem 1. Ising model simulation studies of the critical wetting transition at the marginal dimension $d = 3$ [5] show only a MF-like divergence for the surface susceptibility in sharp contrast to predictions of strong non-classical and non-universal criticality [6] or weakly first-order behavior [4] based on the interfacial model (Eq. (2)).

Problem 2. Ising model simulation studies of the complete wetting transition [7] also in $d = 3$ show that the value of the adsorption critical amplitude θ appearing in the growth law,

$$\kappa\langle l \rangle \approx \theta \ln|\bar{h}|^{-1} \tag{5}$$

is larger than the prediction [8]

$$\theta = 1 + \frac{\omega}{2} \tag{6}$$

based on Eq. (2). Here ω is the usual wetting parameter (see below), the temperature dependence of which is accurately known for the Ising model [9].

Problem 3. MF studies of the pair correlation function at wetting [10] based on Eq. (1) show intriguing features for particle positions near the wall that cannot be understood using the standard effective Hamiltonian (Eq. (2)).

After addressing these concerns we shall show the utility of the new techniques by applying them to a number of other problems of interest in the theory of inhomogeneous fluids.

2. Coupling hypothesis and the CFRS

The starting point for the new effective Hamiltonian theory is the following physical hypothesis [3]:

The problems of wetting theory described above relate to the inability of the standard interfacial model to account for the coupling between order parameter fluctuations near the wall and $\alpha\beta$ interface.

We begin by addressing problem (3) and describe the correlation function reconstruction scheme (CFRS) which allows one to precisely recover the MF order parameter correlation function (at specific positions) using a theory based on collective coordinates. We will take the most general situation [11] and specialize to specific examples later as necessity dictates.

Our first task is to define the collective coordinates upon which our effective theory is based. In general, there may be any number of them (e.g., N say) which prescribe different types of constraint on the underlying magnetization field. In fact, no more need be said at this stage and we can proceed to the next step of performing a constrained functional integral (or partial trace) over magnetization configurations which respect the distribution of the collective coordinates denoted $\{X_\mu(\boldsymbol{y})\}$. Following Fisher and Jin [4] we suppose that our choice of collective coordinates are sensible so that a saddle-point identification is possible:

$$H[\{X_i\}] = \min_{\mathrm{C}} H_{\mathrm{LGW}}[m] \tag{7}$$

where C denotes the particular set of constraints employed. Restricting our attention to long wavelength fluctuations in the fields, the general form of the Hamiltonian is

$$H[\{X_i\}] = \int \mathrm{d}y \left\{ \frac{1}{2} \Sigma_{\mu\nu}(\{X_i\}) \nabla X_\mu \cdot \nabla X_\nu + W(\{X_i\}) \right\} \tag{8}$$

where $W(\{X_i\})$ is the generalised binding potential and the $\Sigma_{\mu\nu}(\{X_i\})$ constitute the elements of the stiffness matrix. Specific expressions for these functions of the $\{X_i\}$ are easily derived in terms of the planar constrained profiles $m_\pi^{(N)}(z;\{X_i\})$ which satisfy a standard Euler–Lagrange equation [11]. Using any one of the effective Hamiltonians we could proceed to study fluctuation effects using, for example, renormalization group (RG) techniques to trace over the remaining degrees of freedom of the fields $\{X_i\}$. Now, in general, different choices of the collective coordinates will lead to different results and physical assumptions are needed to justify a particular approach. For example, if we follow the usual line of reasoning and assume that the only fluctuations that matter are those in the position of the $\alpha\beta$ interface, then we can recover the standard Hamiltonian (Eq. (2)) on adopting a crossing criterion definition for the field $X_1 = l(\boldsymbol{y})$ as the surface of fixed magnetization $m^X = 0$ (say)

[4]. For the moment, however, let us keep our theory as general as possible and quote the central result of the CFRS [11].

For arbitrary choices of the collective coordinates $\{X_i\}$, the multi-field Hamiltonian can recover the MF expression for the transverse Fourier transform of the pair correlation function at the positions $\{z_i\}$ of the fields $\{X_i\}$ according to the invariant relation,

$$G(z_i,z_j;\boldsymbol{q}) = \frac{\partial m_\pi}{\partial X_\mu}(z_i;\{X\})\frac{\partial m_\pi}{\partial X_\nu}(z_j;\{X\})\mathbf{S}_{\mu\nu}(\boldsymbol{q}) \tag{9}$$

where $\mathbf{S}_{\mu\nu}$ is the matrix of structure factors,

$$\mathbf{S}_{\mu\nu}(\boldsymbol{q}) = \int \mathrm{d}\boldsymbol{y} \mathrm{e}^{iq\cdot(y_2-y_1)}\big(\langle X_\mu(\boldsymbol{y}_1)X_\nu(\boldsymbol{y}_2)\rangle - \langle X_\mu\rangle\langle X_\nu\rangle\big). \tag{10}$$

This may be calculated using the stiffness matrix expression [12]

$$\mathbf{S}^{-1}(\boldsymbol{q}) = \begin{pmatrix} \partial_{11}^2 & \partial_{12}^2 \cdots \\ \partial_{12}^2 & \partial_{22}^2 \\ \vdots & \end{pmatrix} W(\{X\}) + q^2\boldsymbol{\Sigma}, \tag{11}$$

where $\partial_{\mu\nu}^2 \equiv \partial^2/(\partial X_\mu \partial X_\nu)$ and is evaluated at MF equilibrium. We emphasise that this procedure is valid for different collective coordinates and that the identifications [9] correspond to the precise solution to the MF Ornstein–Zernike equation (with $\tilde{m}(z)$ the MF profile) [10],

$$(-\partial_z^2 + \phi''(\tilde{m}(z)) + q^2)G(z,z';\boldsymbol{q}) = \delta(z-z') \tag{12}$$

at the specific points $z,z' \in \{z_i\}$. This theorem provides the necessary mathematical framework for the solution to problem (3) and it only remains for us to choose suitable coordinates to describe the correlation function structure at a given transition.

2.1. Example: correlation structure at complete wetting

For this transition the inhomogeneity in the magnetization at the wall is large and following Parry and Boulter [13], we can define interfacial-like variables $X_1(\boldsymbol{y}) = l_1(\boldsymbol{y})$ and $X_2(\boldsymbol{y}) = l_2(\boldsymbol{y})$ corresponding to surfaces of fixed magnetization that remain bound and unbound from the wall, respectively, as $\bar{h} \to 0$. The Hamiltonian for this coordinate system is

$$H[l_1,l_2] = \int \mathrm{d}y \left\{ \frac{1}{2}\Sigma_{\mu\nu}(l_1,l_2)\nabla l_\mu \cdot \nabla l_\nu + \frac{1}{2}r\ell_1^2 + W(l_{21}) \right\}, \tag{13}$$

with $W(l_{21}) \equiv W(l_2 - l_1)$ similar to the standard result (Eq. (3)). The stiffness matrix reads

$$\boldsymbol{\Sigma} = \begin{pmatrix} \Sigma_{11} & 0 \\ 0 & \Sigma_{\alpha\beta} \end{pmatrix} + 2m_\alpha \kappa^2 \tau l_{21} \mathrm{e}^{-\kappa l_{21}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \cdots \tag{14}$$

and shows that the leading-order position dependence is carried by the off-diagonal elements. The Σ_{11} term can be explicitly related to the surface tension of the wall–α interface [13]. For the present interfacial coordinates the fundamental CFRS equation simplifies to [12]

$$G(z_i, z_j; \boldsymbol{q}) = \tilde{m}'(z_i)\tilde{m}'(z_j)S_{ij}(\boldsymbol{q}). \tag{15}$$

For positions $z_i,\ z_j = \langle l_2 \rangle$ rangle, close to the $\alpha\beta$ interface, this reproduces the well known Ornstein–Zernike-like simple Lorentzian form of the pair correlation function. Near the wall, however, the solution is of the required non-Lorentzian form,

$$G(0,0;\boldsymbol{q}) = \frac{\tilde{m}_1'^2}{r + q^2\left[\Sigma_{11} + \dfrac{\Sigma_{22} + 2\Sigma_{12}}{1 + q^2\xi_{\|}^2}\right]} \tag{16}$$

seen in the MF studies [10]. By construction this is fully consistent with the explicit solution to the MF Ornstein–Zernike equation (Eq. (12)) which had caused so much trouble within the standard interfacial Hamiltonian theory. One of the elegant features of this approach is the stiffness-matrix free energy relation,

$$f_{\text{sing}} \approx 2\Sigma_{12}, \tag{17}$$

which ensures that the formalism is consistent with an exact sum-rule requirement. Note that the position dependence of the r.h.s. correctly identifies the singular contribution to the surface free energy.

3. Fluctuation effects; optimized coupled theory

To consider fluctuation effects beyond MF, we must carefully choose our collective coordinates. With our starting point, the coupling hypothesis, we seek to derive a two-field Hamiltonian which describes the interactions of the large fluctuations in the position of the $\alpha\beta$ interface described by an interfacial-like variable $X_2 = l$ with the relatively small fluctuations of the magnetization near the wall. The choice of collective coordinate X_1 for the lower field is not as obvious, and it is best to consider a space of Hamiltonians [11,14],

$$\mathscr{H} = \{H[s, l; \delta]\} \tag{18}$$

characterized by a proper collective coordinate s and coupling angle δ (see Fig. 1). The proper collective coordinate has spin-like and interfacial-like components as can be seen in the fundamental constraint equation [14],

$$m(s\cos\delta) = m_{\text{FJ}}(0; l) + \kappa m_{\alpha} s \sin\delta, \tag{19}$$

where $m_{\text{FJ}}(z; l)$ denotes the Fisher–Jin profile which does not account for coupling effects [3,4]. The simple geometric meaning of the coupling angle δ is shown in figure 4.2 taken from Ref. [14].

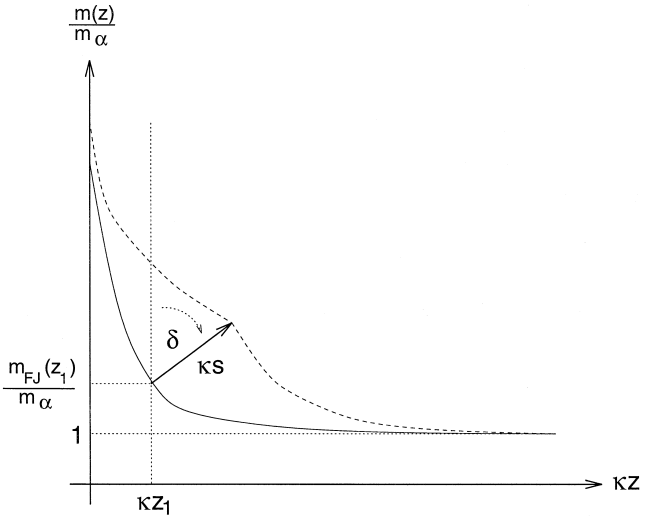

Fig. 1. Detail of the planar magnetization profiles near the wall in scaled units. The broken curve shows $m(z)$ which incorporates a local enhancement and translation of the FJ profile (corresponding to the solid line). The proper coordinate s and angle δ are shown.

We then ask which choice of Hamiltonian in $\mathscr{H}$ is best for modelling the small order parameter fluctuations near the wall? Using the CFRS described above, it is straightforward to establish that the optimal choice corresponds to a coupling angle [14],

$$\tan \delta * = - \frac{\left.\frac{\partial m_{\rm FJ}}{\partial z}\right|_{z=0}}{\kappa m_\alpha} \approx \frac{\tau}{m_\alpha}, \tag{20}$$

since this has the largest local binding potential curvature and stiffness coefficient Σ_{11} [11]. Thus, deep in the complete wetting regime, $\delta * = \pi/2$ and the proper collective coordinate is interfacial-like similar to the model (Eq. (13)). However, as the temperature is reduced to the critical wetting boundary ($\tau = 0$), the coupling angle rotates and eventually vanishes. Thus, near the critical wetting transition, the proper field s has no interfacial component and is a spin-like variable [11,14]. In general, the optimal coupled Hamiltonian has the form (ignoring the position dependence of the stiffness coefficients) [14],

$$H[s,l] = \int \mathrm{d}\boldsymbol{y} \left\{ \frac{1}{2}\Sigma_{11}^W \sec^2\delta * (\nabla s)^2 + \frac{1}{2}\Sigma_{\alpha\beta}(\nabla l)^2 + \frac{1}{2}\bar{r}s^2 + W(l - s\sin\delta *) \right\} \tag{21}$$

and is amenable to RG analysis [15]. Here Σ_{11}^W is independent of τ and is explicitly determined. In many respects the predictions for fluctuation effects are similar to those of the simpler one-field model(s) but there are notable differences. Firstly, for the complete wetting transition, the value of the adsorption critical amplitude θ (Eq. (6)) is renormalized due to coupling effects [14,15],

$$\overline{\omega} = \omega + \Omega \frac{(\tau/m_\alpha)^2}{1 + (\Lambda \xi_{w\alpha})^{-2}} + O\left((\tau/m_\alpha)^4\right), \tag{22}$$

which should be compared with the standard result (Eq. (6)) which does not have the final term. In this expression $\xi_{w\alpha}$ denotes the correlation at the wall–α interface and Λ is a suitable momentum cut-off (of order of an inverse bulk correlation length or lattice spacing). Eq. (22) shows the role played by two wetting parameters

$$\omega = \frac{k_B T \kappa^2}{4\pi \Sigma_{\alpha\beta}}; \quad \Omega = \frac{k_B T \kappa^2}{4\pi \Sigma_{11}^W} \tag{23}$$

in contrast to the standard theory equivalent to $\Omega = 0$. In fact, we estimate [11] that Ω approaches a universal value $\Omega_c \approx 0.92$ in the bulk critical region complementing the expected universality of ω [9].

In application to the critical wetting transition the optimal model shows the same asymptotic singularities as the standard model but the size of the critical regime is dramatically reduced. Calculation of the Ginzburg criterion shows that cross-over to non-classical behavior occurs when the (diverging) transverse correlation length $\xi_{\|}$ is close to a value satisfying [14]

$$\Lambda \xi_{\|} \approx e^{1+\omega^{-1}} \left(1 + \Lambda^2 \xi_{w\alpha}^2\right)^{\frac{\Omega}{\omega}} + \cdots, \tag{24}$$

which is about an order of magnitude bigger than the standard interfacial Hamiltonian result [16].

Eqs. (22) and (24) are the main results of the optimal model calculation and offer quantitative explanation of the remaining problems (1) and (2).

4. Other applications

4.1. Correlation function algebra

Using the general CFRS (Eq. (9)), it is possible to investigate correlation function structure for local density functional models of fluid confinement in parallel-plate geometries. Equivalently we may regard these as pertinent to the correlation functions of the LGW model in MF approximation for the more general situation where a second surface is present at $z = L$. For arbitrary positions $0 \le z_1 \le z_2 \le z_3 \le L$ let us define the variables,

$$S_{\mu\nu} = \frac{G(z_\mu, z_\nu; 0)}{\tilde{m}'(z_\mu)\tilde{m}'(z_\nu)}. \tag{25}$$

By considering the properties of general three-field Hamiltonians $H[l_1, l_2, l_3]$ with interfacial-like variables, we can show [17] that the algebraic relations,

$$S_{12} S_{23} = S_{22} S_{13} \tag{26}$$

$$(S_{11} - S_{12})(S_{33} - S_{23}) = (S_{13} - S_{12})(S_{13} - S_{23}) \tag{27}$$

must be obeyed. These conditions constrain the form of the correlation function in parallel-plate geometries. For example, for the case of confinement between identical walls, we can derive [17]

$$\sigma(z_1, z_2) = \left(1 \pm \sqrt{1 - \sigma(z_1, z_1)}\right)\left(1 \pm \sqrt{1 - \sigma(z_2, z_2)}\right), \tag{28}$$

where

$$\sigma(z_\mu, z_\nu) = 4\frac{\mathrm{d}^2\gamma}{\mathrm{d}L^2}\frac{G(z_\mu, z_\nu; \boldsymbol{q})}{\tilde{m}'(z_\mu)\tilde{m}'(z_\nu)}. \tag{29}$$

Here, $\gamma(L)$ is the finite-size surface free energy and the $\pm$ signs depend on whether $z_\mu < L/2$ or $z_\mu > L/2$, respectively. This is an explicit expression for the correlation between two planes in terms of the correlations along them. Using this relation we can rederive non-trivial expressions for the scaling of the free energy associated with confinement near the bulk critical point and in the presence of strong interfacial fluctuations.

4.2. Wetting at non-planar walls

Finally we note that the stiffness matrix formalism helps us analytically solve the problem of wetting at a non-planar wall in MF approximation. One can construct a linear response theory which relates the free energy of the non-planar system to the correlation functions of the planar geometry [18]. Specifically let us consider a LGW Hamiltonian but with the wall located at $z_W(\boldsymbol{y})$ and with an extra multiplicative surface term related to the increase in area. For small deviations from the plane it is natural to write the MF free energy as

$$F = \phi(m_{\mathrm{bulk}})V + \sigma A_\pi + \frac{1}{2(2\pi)^{d-1}}\int \mathrm{d}\boldsymbol{q}\, q^2\Delta_\pi(q)|\hat{z}_W(\boldsymbol{q})|^2 + \cdots, \tag{30}$$

where σ is the surface tension and $\hat{z}_W(\boldsymbol{q})$ are the Fourier components of $z_W(\boldsymbol{y})$. The quantity to be determined describing the non-planar correction to the free energy is $\Delta_\pi(q)$ and using the CFRS we can show [18]

$$q^2\Delta_\pi(q) = q^2\phi_1(\tilde{m}_1) + \tilde{m}_1'^2\left(\frac{1}{G(0,0;q)} - \frac{1}{G(0,0;0)}\right), \tag{31}$$

where the correlation function is for the planar geometry. These equations are amenable to an elegant graphical analysis [18] allowing us to analytically determine the influence of the non-planar boundary on wetting transitions. For strongly first-order phase transitions the wetting transition temperature is lowered consistent with the predictions of a simple phenomenological argument [18]. For second-order wetting transitions, however, the effect of the boundary geometry is more subtle and the transition is generically roughness-induced first-order provided the width of the undulations is larger than a bulk correlation length. This again illustrates the sensitivity of wetting transitions to 'fluctuation' effects at least above and at the upper critical dimension $d = 3$.

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